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New absorption band spectra of the hydrogen molecule in the extreme ultraviolet region

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NEW ABSORPTION BAND SPECTRA OF THE HYDROGEN MOLECULE IN THE EXTREME ULTRAVIOLET REGION

by

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NEW ABSORPTION BAND SPECTRA OF THE HYDROGEN MOLECULE IN THE EXTREME ULTRAVIOLET REGION

INTRODUCTION

The $3p'\Pi_{cd} - 1s'\Sigma$ band system of the hydrogen molecule was discovered in absorption by Hopfield[1] who observed a single progression of bands extending from about 848 Å and extending to shorter wave lengths. He assumed the first (longest wave lengths) to be the 0-0 band of the system as is ordinarily the case. Beutler, Deubner and Junger[2], and Beutler and Junger[3], by means of the isotope effect showed that Hopfield's absorption progression began with the v = 3 level of the upper state, provided their analysis of the heavy hydrogen bands is assumed correct. This had previously been suggested by Richardson[4] as a possible explanation of the bands, since the heat of dissociation and Rydberg denominator indicated by this progression were not compatible with other known data on H_2, if the first member of the progression were the 0-0 band. The appearance of the higher members of the absorption bands discovered by Hopfield and the absence of the 0-0, 1-0, and 2-0 bands has been explained as due to pre-dissociation of the molecule in the higher vibrational levels of the $3p'\Pi_{cd}$ state and their consequently greater strength in absorption. Due to pre-dissociation the bands were broad and diffuse and the molecular constants could not be derived from them. A few

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1 J. J. Hopfield, Nature 125, 927 (1930).

2 Beutler, Deubner and Junger, Zeits. f. Physik 98, 181 (1935).

3 Beutler and Junger, Zeits. f. Physik 100, 80 (1936).

4 O. W. Richardson, Molecular Hydrogen and its Spectrum, (Yale University Press, 1934) 303.

of the bands of this system for v = 0, 1 and 2 in the upper state were discovered by Jeppesen[5] in emission.

In order to obtain more data on the molecule and give further verification of the analysis by the above mentioned workers, it is desirable to discover the absorption bands having v = 0, 1 and 2 in the $3p'\Pi_{cd}$ state. The discovery and identification of these bands are described in the following paragraphs.

EXPERIMENTAL PROCEDURE

Method of Producing $3p'\Pi_{cd} - 1s'\Sigma$ Bands

The desired bands (see Figure 2) appear in absorption only at a particular pressure. This pressure is found to be slightly greater than 10^{-1} mm. of mercury. At a pressure greater than this the absorption is too great, absorbing the continuum, thereby limiting the extent of the spectrogram in the ultraviolet short of the point where the bands are calculated to be. Figure 1 is a spectrogram obtained under these conditions showing the continuum absorbed beyond 1030Å. It is found that at a pressure of 10^{-1} mm. of mercury a few absorption lines appear but at any pressure

Figure 1

less than this value no absorption lines appear that can be classified as belonging to the 0-0, 1-0, or 2-0 bands, as is shown in Figure 3.

5 C. R. Jeppesen, Physical Review 54, 68 (1938)

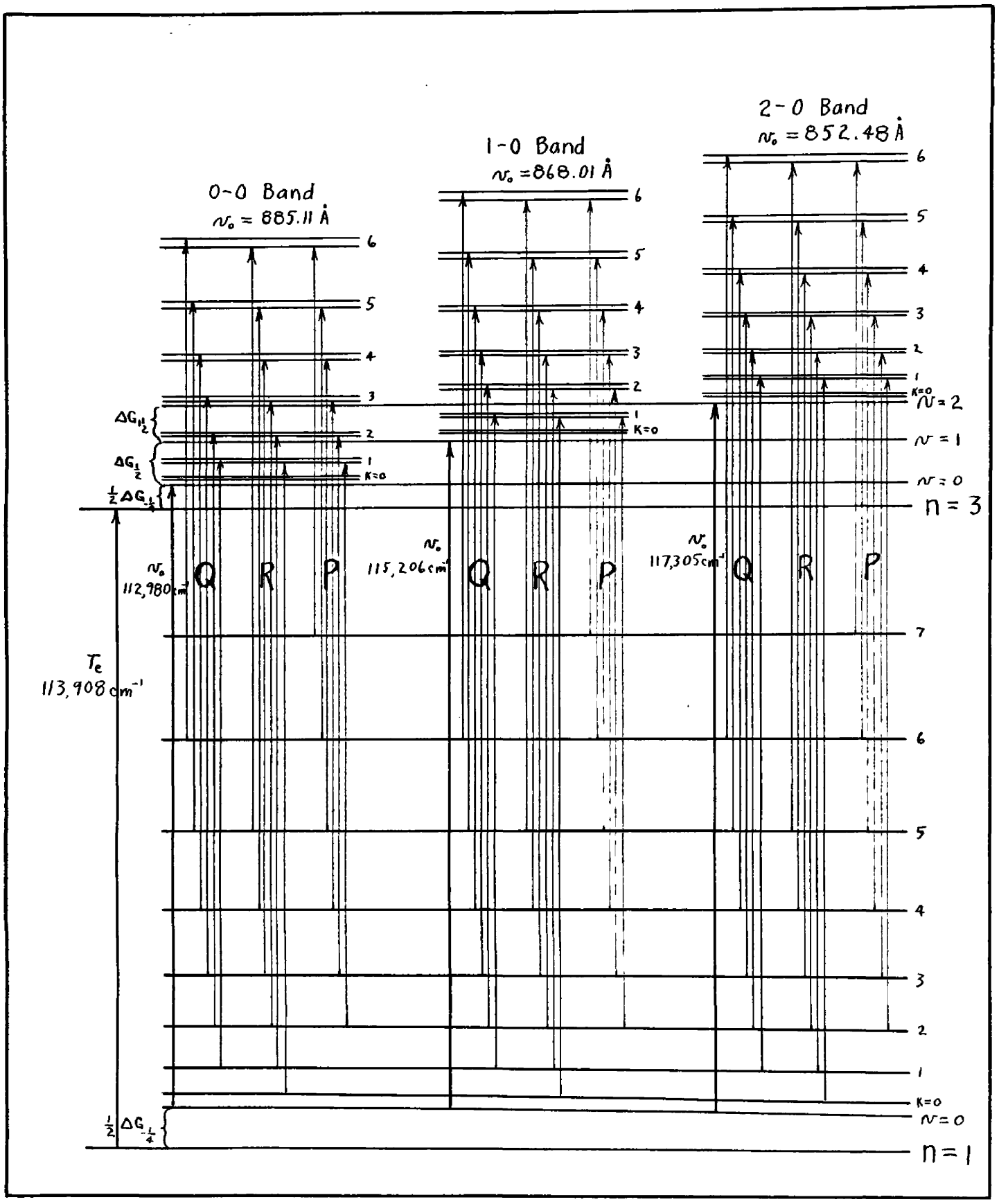

Fig. 2
Energy Level Diagram of
$3p'\Pi_{cd} - 1s'\Sigma$ Bands

Figure 3

The continuum may be produced by means of the discharge of a high voltage condenser through a spark-gap in series with the discharge tube, a method similar to that used by Collins and Price[6]. The discharge taking place in the tube is caused to pass through a capillary about 2.5 cm. long with an internal diameter of 1 mm. This causes a very heavy density, and by reducing the inductance in the discharge circuit to a minimum, a very heavy spark of high energy may be obtained. It is believed that the continuum is produced by radiations from the particles of ionized glass that are blown from the interior of the capillary.

A slight amount of gas, in this case hydrogen, is necessary to preciptate the discharge. It is found that a pressure of 10^{-3} mm. of mercury is sufficient to produce a good discharge.

The extent of the continuum toward the ultraviolet is directly proportional to the potential of the discharge, while the intensity of the spectrum is directly proportional to the capacity of the condenser. Collins and Price using 15,000 volts with a capacity of 1.5 μf were able to obtain a continuum down to around 300 Å. With the apparatus used in this experiment the continuum extends to 700 Å. using a capacity of .5 μf and a potential of 11,000 volts. The present study indicates that with a circuit containing very low inductance, a capacity of 1 μf and potential of 11,000 volts, produces too great an amount of energy and the capillary of the discharge tube is most always shattered. A potential of 11,000 volts and

6 Collins and Price, Review of Scien. Inst. 5, 423 (1934).

always shattered. A potential of 11,000 volts and capacity of .5 μf produces a satisfactory continuous spectrum for use in the region of the present study.

Construction of the Apparatus

The principal items of apparatus used are the spectrograph, the discharge tube, the vacuum system and the power supply. The function of each of these parts will be described in the following paragraphs. The connection and assembly may be seen in Figure 4 and 5.

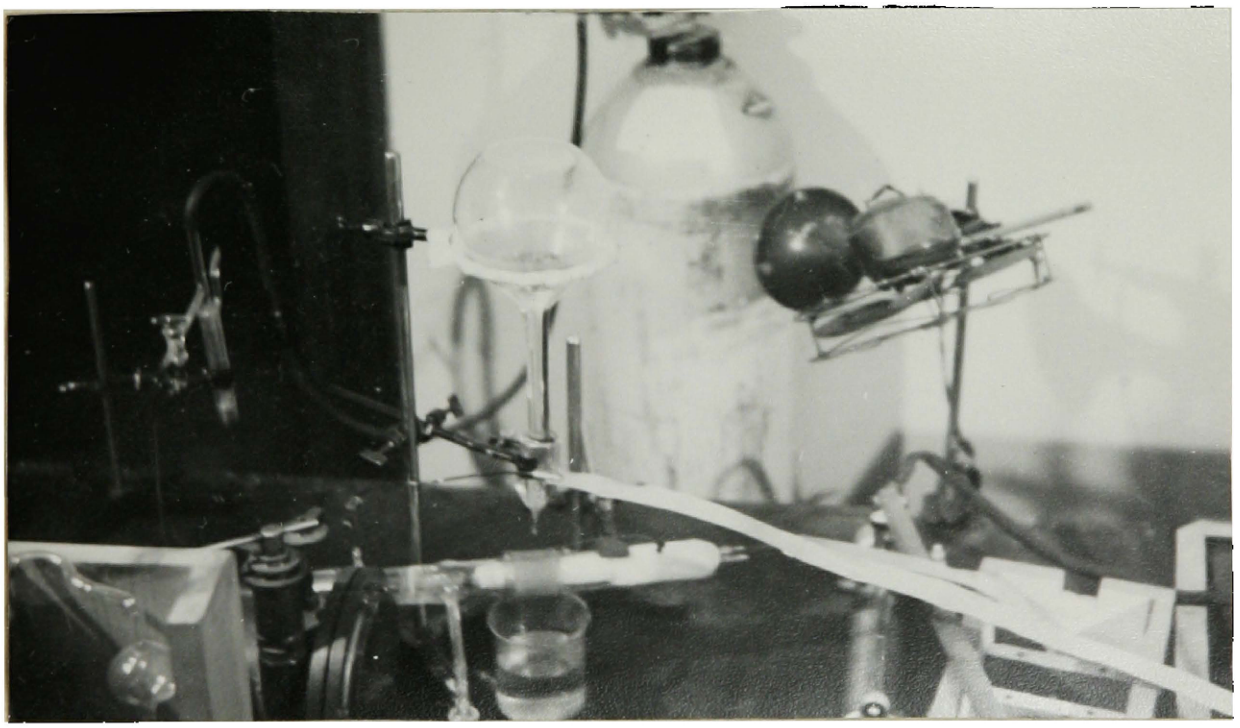

Figure 4 Assembly of Apparatus

The high energy spark that passes through the tube at the rate of 120 discharges per minute at 11,000 volts wears away the capillary to double the original diameter after 45 minutes of operation. Therefore it is necessary to construct the tube in such a way that the capillary is easily replaceable. This is accomplished by making the tube with a taper fitting, thus making it possible to replace the capillary with a minimum amount of work. Figure 6

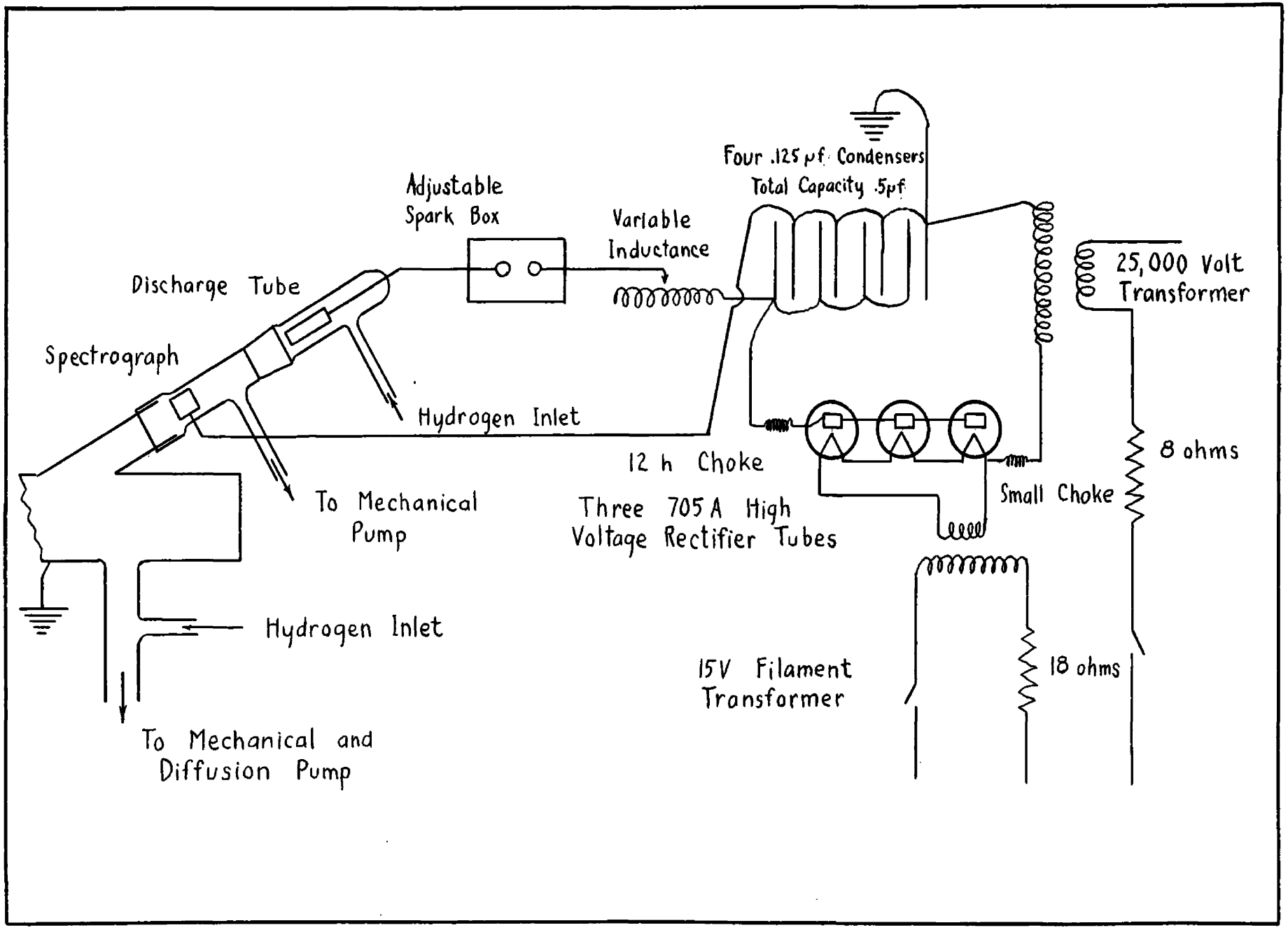

Fig. 5

Skematic Diagram of Experimental Arrangement

shows a view of the tube as it fits on the spectrograph. Hydrogen may

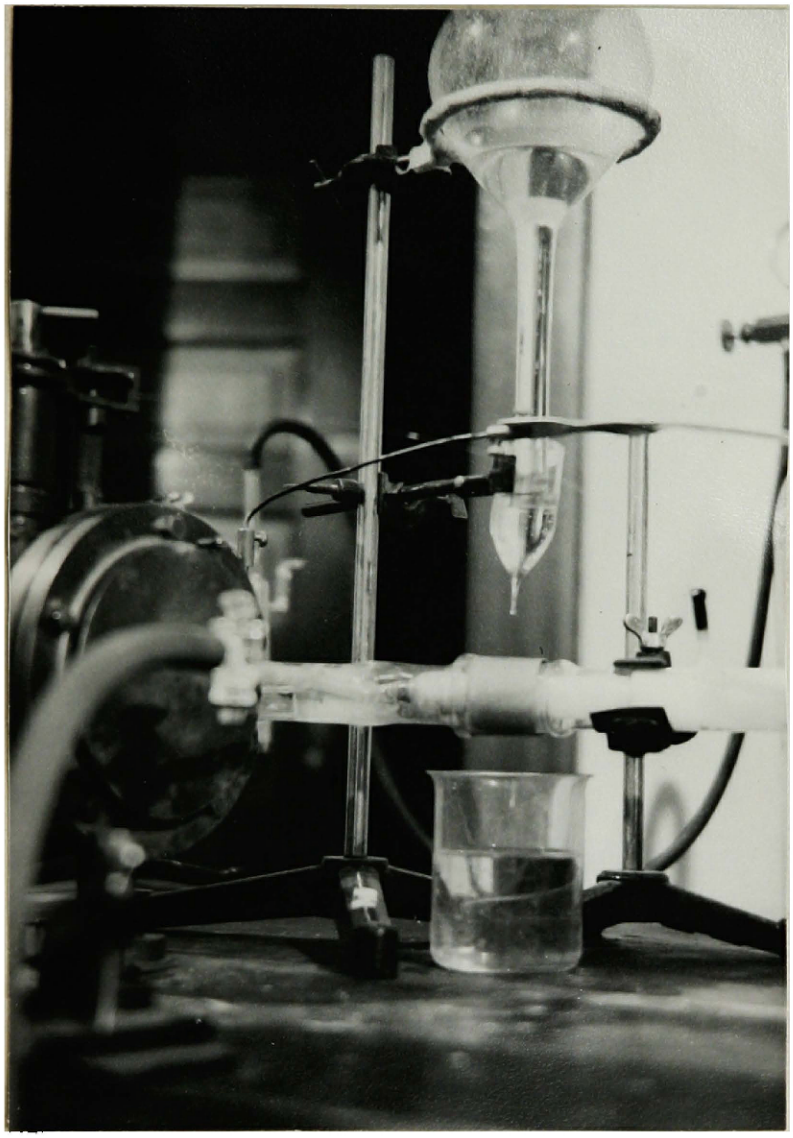

Fig. 6 Photograph of Discharge Tube

admitted to the tube through a fine capillary leading into the rear section of the tube. The air is evacuated by means of a mechanical pump through an outlet in the fore section of the tube as is indicated in Figure 7. The taper fitting is special ground glass, and is made air tight by coating the surface of the taper with vacuum stopcock grease. The taper fitting surrounds one of the electrodes and therefore is subjected to fairly high temperature. To prevent the grease from becoming liquid, and allowing air

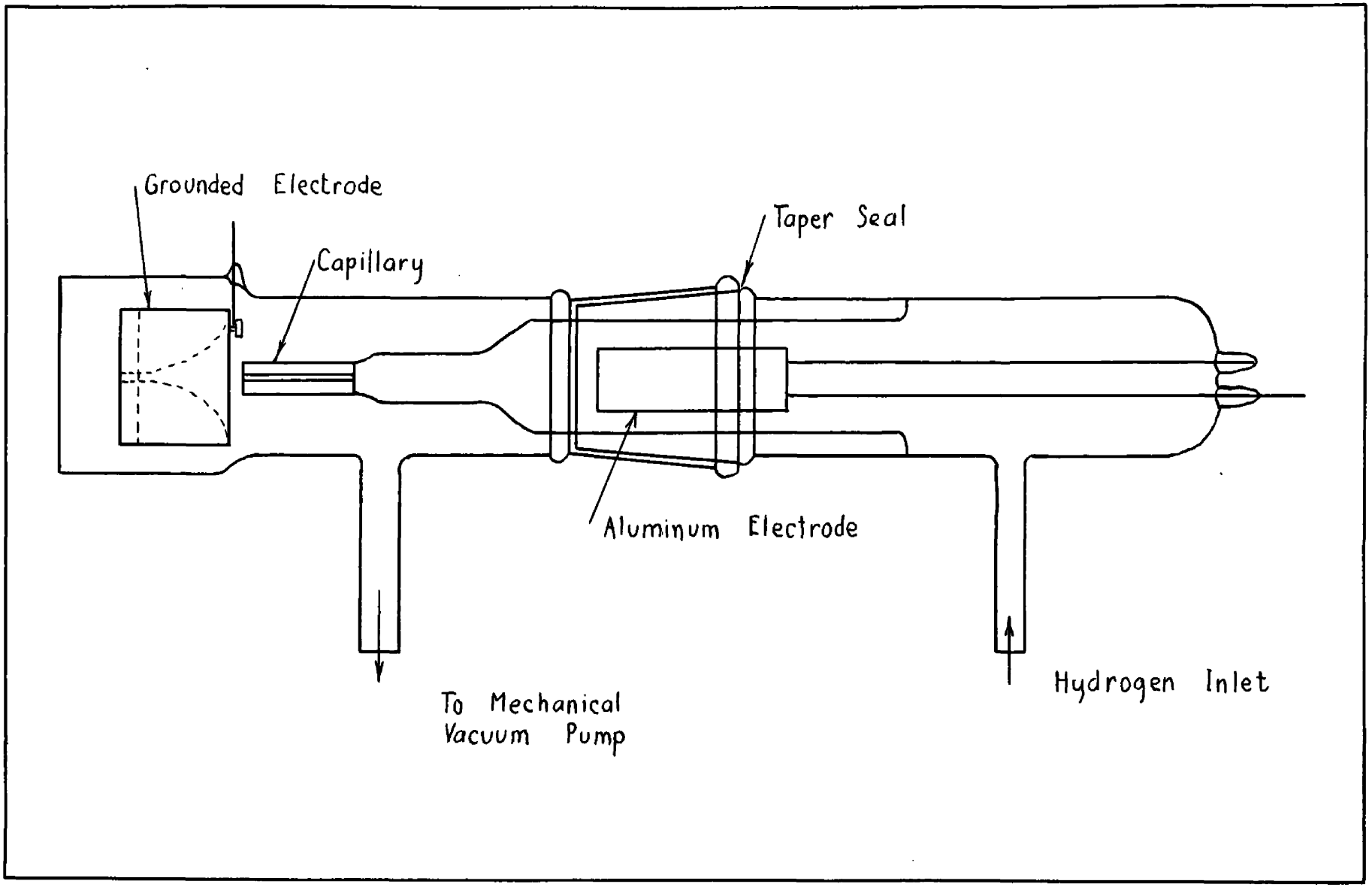

Fig. 7
Diagram of Discharge Tube

bubbles to leak in, the taper fitting is kept cool by means of a steady flow of cold water allowed to run over a wick which is wrapped around the tube at that point.

The electrodes are both made of aluminum. The high voltage electrode is made of a strip of sheet aluminum rolled into a cylinder and connected to the exterior of the tube by tungsten wire. The grounded electrode is also made of aluminum, but is of a special design as shown in Figure 8.

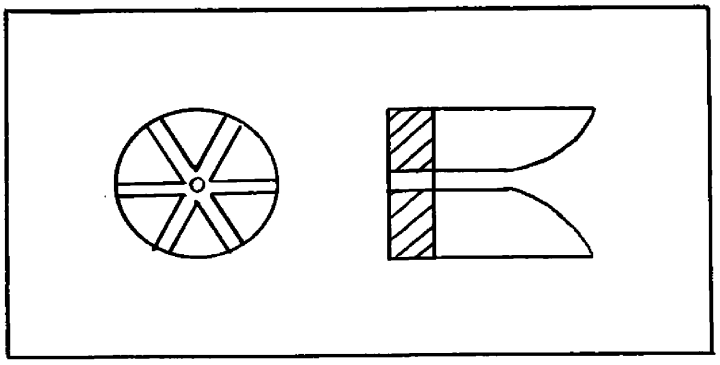

Figure 8 Diagram of Grounded Electrode

This construction permits the use of the strong electric field that exists near sharp edges of charged bodies to trap the high speed glass ions before they are projected through the slit.

The hydrogen is obtained from a high pressure tank and, by means of a series of stepdown valves, is supplied to the discharge tube and spectrograph through small capillaries. The pressure in the system may be regulated by using capillaries of various diameters, the lengths being arbitrary since the length does not affect the pressure. The hydrogen necessary to operate the discharge tube is delivered by a capillary .0142 cm. in diameter. The hydrogen absorption takes place in the spectrograph where the absorbing gas is supplied through a second capillary .0279 cm. in diameter.

In operation the apparatus is first evacuated to an air pressure less than 10^{-5} mm. of Hg. The apparatus used for evacuation consists of two Cenco mechanical oil pumps, and a mercury diffusion pump. One of the mechanical pumps is used to evacuate the tube. The other mechanical pump assisted by the diffusion pump maintains a vacuum in the spectrograph.

The spectrograph used was designed by Dr. C. R. Jeppesen, and was constructed by the instrument shop of the University of California Physics department. The slit width, adjusted by hand before the system is evacuated, is estimated by eye. An air tight bearing makes it possible to adjust the film holder while the apparatus is in operation. Five exposures may be taken on a single film.

The concave grating was ruled at the Johns Hopkins University shop. It is made of flint glass, ruled with 11,800 lines per cm., and has a focal length of 42 cm. which gives a dispersion of about 20 Å per mm.

It is necessary to use Schumann[7] type film for the photographing of the spectrum because the gelatin on ordinary film absorbs the radiations in the ultraviolet region.

A photograph showing the parts of the electrical system is shown in Figure 9. Reference may also be made to Figure 5. As was mentioned earlier a high voltage spark with a minimum amount of inductance is required for the production of a good continuum.

The high voltage is furnished by a 25,000 volt transformer. The current in the secondary being controlled by adjusting a resistance in the primary. Satisfactory results are obtained by use of a resistance of 7 ohms.

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7 J. J. Hopfield and Appleyard, Jour.Opt. Soc.Am.,22 (1932).

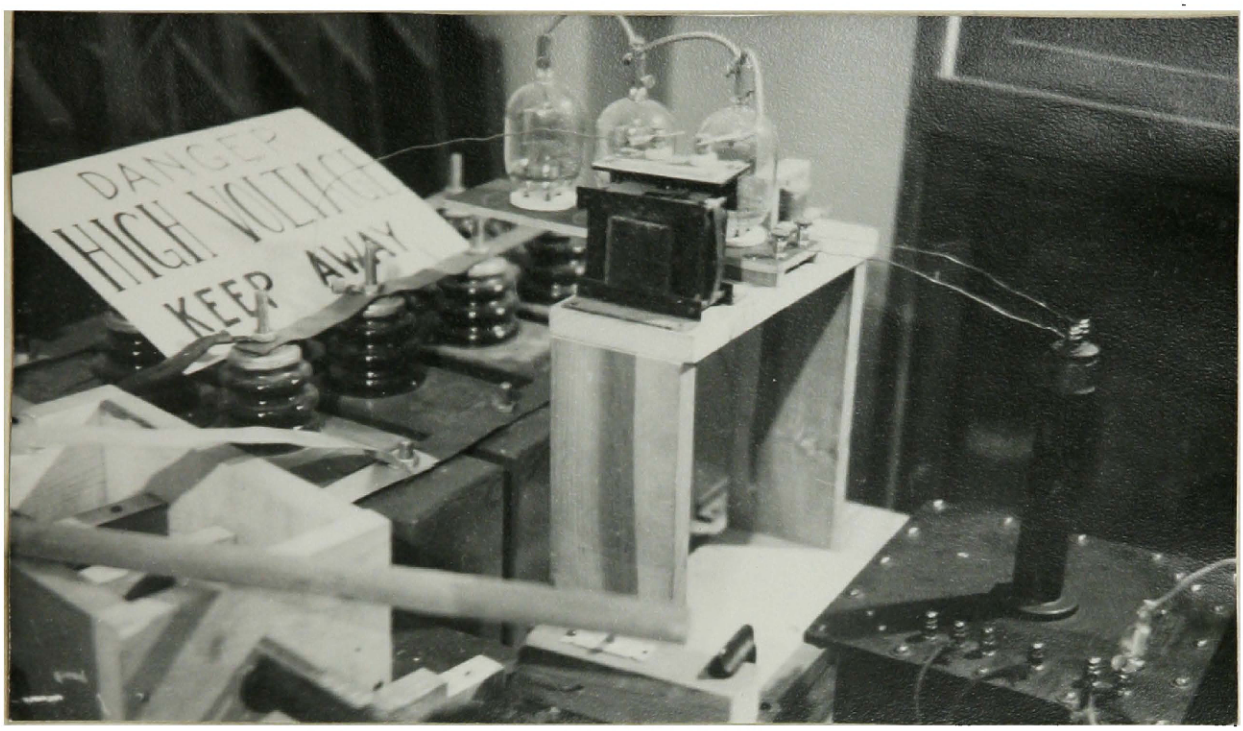

Figure 9 Electrical System

The current is rectified by means of three 705 A high voltage rectifier tubes connected in parallel. Three tubes are used in order to increase the rate of discharge so that cooling of the capillary in the discharge tube cannot occur between discharges. The tube filaments are operated from a 15 volt high voltage insulated filament transformer supplying 15 amps. The tubes are protected from high frequency oscillations by a choke on either side of the tube assembly.

The rectified current charges four condensers insulated up to 27,000 volts, each with a capacity of .125 μf giving a total capacity of .5μf.

The potential of the discharge is regulated by an adjustable spark box calibrated to read the gap in mm. Table I shows values of potentials for corresponding values of the spark gap distance. An adjustable inductance is placed in series with the spark box so that inductance can be put

Spark Gap cm.	1 cm. diam. Balls D. C. Voltage
0.1	5,000
0.3	11,000
0.6	20,000
1.0	27,000
2.0	36,000
4.0	45,000

Table I
Sparking Potentials

in the circuit while the tube is being warmed up, and totally removed while an exposure is being taken. The spark box is operated with an open top so a fan can circulate the air in the box to prevent irregular discharges due to ionized air.

Care was taken in laying out the electrical diagram so that the discharge circuit contained a minimum amount of inductance.

Photography of the Bands

As previously mentioned the pressure and potential were the critical variables in producing the desired absorption bands. A great many trials were made before the proper pressure and potential was found.

Production of the continuum is another source of difficulty in this experiment. It is found that in order to avoid too strong absorption in the discharge tube itself the distance from the end of the capillary to the slit must not be too great. A distance of 7 cm. was found to be too much. Results are obtained with this distance equal to about 3 cm., but a shorter distance is probably more satisfactory.

The small amount of air remaining in the system plus the oxygen

8 Stewart, Physics, 437.

liberated by the hot glass from the capillary caused the appearance of line spectra of nitrogen and oxygen making it possible to use these lines as standards in measuring the absorption bands accurately..

EXPERIMENTAL RESULTS

Absorption Bands Obtained

Examination of the spectrogram obtained by the methods described results in the determination of the wave lengths of 74 absorption lines between 852 Å and 905 Å. Of these 74 lines, 41 were identified as belonging to the three desired bands. Several of these lines are broad, indicating the presence of two or more lines where only one could be measured. Figure 10 shows an enlarged photograph on the spectrogram.

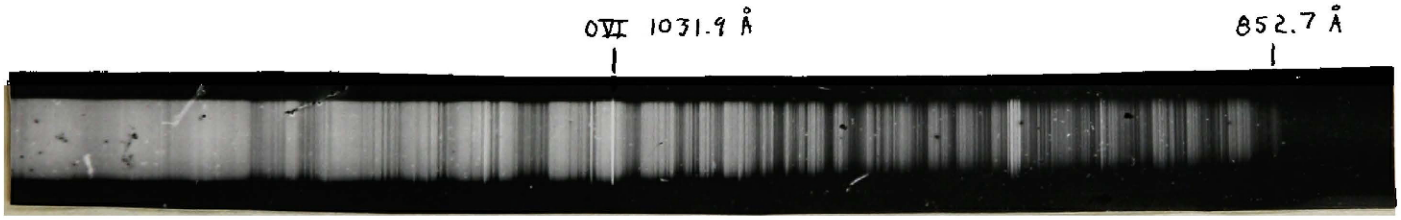

Figure 10

Wave Lengths of Standards

The afore mentioned nitrogen and oxygen lines that appear in emission affords excellent lines to be used as standards. The wave lengths listed in the tables are determined with respect to five of these standard lines which are recorded in Table II

Table II
Wave Length of Standards

Spectrum	Int.	λ	Obs. λ	Diff.
O III	2	898.956	896.70	-2.26
O IV	4	921.301	919.06	-2.24
N IV	10	921.982	919.69	-2.29
N IV	10	922.507	920.20	-2.31
N IV	10	924.274	922.09	-2.18

The wave length of any line on the spectrogram is given by the linear dispersion equation $\lambda = 19.787x + 0.005891x^2 - 0.000025^3$ where x is the distance in mm. of a line from the central image. Measurement of the line results in a discrepency of over two Angstroms between the true value of the standard wave lengths and their wave lengths as calculated from the measurements by use of the dispersion equation. This is due to the broadness of the central image and to the shrinkage of the film. The last value recorded in Table II is disregarded and the average difference is taken using the other four values. This gives a value of -2.28 Å which is then added to all measured wave lengths as determined by the linear dispersion equation.

Results and Conclusions

Assuming Jeppesen's analysis of the emission spectrum to be correct the wave number of each line in the absorption bands can be calculated. Table III gives the important constants of the $3p'\Pi_{cd}$ and $1s'\Sigma$ states from the above analysis.

Table III[9]

T_e	113908 ± 10 cm^{-1}
$\frac{1}{2}\Delta G_{-\frac{1}{4}}$ for	$3p'\Pi_{cd}$ state, 1148 cm^{-1}
$\frac{1}{2}\Delta G_{-\frac{1}{4}}$ for	$1s'\Sigma$ state, 2176 cm^{-1}

Using these constants the rotational energy of each state is found by calculation to be as given in Table V.

Table IV gives the observed wave length and the calculated wave length of each line of the three bands. The difference in observed and calculated value is given in the column O-C.

9 Jeppesen, Loc. Cit.

Table IV

Bands of the $3p'^1\Pi_{cd} - 1s'^1\Sigma$ System[10]

Q Branches				R Branches				P Branches			
K'	calc λ	obs λ	O-C	K'	calc λ	obs λ	O-C	K'	calc λ	obs λ	O-C
				0-0 Band v_o = 885.11 Å							
1	885.88			1	884.96	885.69*	.73	1	887.74	887.47	-.27
2	887.25			2	885.43			2	890.04	889.78*	-.26
3	889.28			3	886.57	886.64*	.07	3	893.01	893.39	.38
4	891.98	892.02	.04	4	888.41			4	896.64	896.32	-.32
5	895.32	895.63	.31	5	890.90	890.85	-.05	5	900.89	901.12*	.23
6	899.27	899.46	.19	6	894.05	894.04	-.01	6	905.78	905.43	-.35
				1-0 Band v_o = 868.01 Å							
1	868.76			1	867.87			1	870.56	870.35	-.21
2	870.09	870.01	-.08	2	868.33	868.42	.09	2	872.78		
3	872.08			3	869.47	869.44	-.03	3	875.67	875.33	-.34
4	874.64	874.50*	-.14	4	871.26	871.00	-.26	4	879.19	879.00*	-.19
5	877.97	877.63	-.34	5	873.71	873.72*	.01	5	883.31	883.62	.31
6	881.83			6	876.79	876.40	-.39	6	888.07	888.09	.02
				2-0 Band v_o = 852.48 Å							
1	853.21			1	852.38			1	854.94	854.79	-.15
2	854.52			2	852.82			2	857.11	857.21	.10
3	856.46	856.30	-.16	3	853.93	853.72*	-.21	3	859.92	859.99	.07
4	859.03	859.10	.07	4	855.70	855.42	-.28	4	863.35	863.48*	.13
5	862.23	862.23*	.00	5	857.91	857.87	-.04	5	867.36	867.43	.07
6	866.00	866.02	.02	6	861.13	861.38*	.25	6	872.01	872.75*	.74

* Indicates broad lines

10 Calculated values are from C.R.Jeppesen's work, Physical Review 54, 68 (1938)

Table V

Value[11] of $F = B(K+\frac{1}{2})^2 + D(K+\frac{1}{2})^4 + F(K+\frac{1}{2})^6$

For $1s\Sigma$ state		For $3p'\Pi_{cd}$ state					
v=	0	0		1		2	
		c	d	c	d	c	d
K=0	14.84						
1	133.31	33.8	35.1	32.4	33.7	31.1	32.3
2	369.19	93.6	97.2	89.9	93.4	86.3	89.5
3	720.30	182.9	190.1	175.9	182.6	168.9	175.1
4	1183.55	301.6	313.4	290.0	300.8	278.3	288.6
5	1754.94	449.1	466.5	431.7	447.7	414.3	429.4
6	2427.77	624.5	648.5	600.5	622.6	576.3	597.1
7	3202.82						

Figures 11, 12 and 13 are Frotrat diagrams of the three bands showing the calculated values plotted in black compared to the position of the observed wave lengths shown in red dots.

In conclusion it may be noted that this investigation has resulted in the discovery of three new absorption bands in the system of hydrogen. These bands have not yet been found in emission. The very accurate check between the measured wave length of the lines of these bands and the values calculated from the results of Jeppesen's analysis of other emission bands shows that the essential correctness of the analysis is unquestionable.

The accuracy of the work is limited by the comparator which measures lines with an error of ±.015 mm., and the spectrograph with a dispersion of 20 Å per mm. With a more accurate comparator, and a spectrograph with a higher dispersion, these lines could be located accurately to ±.005 Å as compared to a ±.3 Å accuracy of this paper.

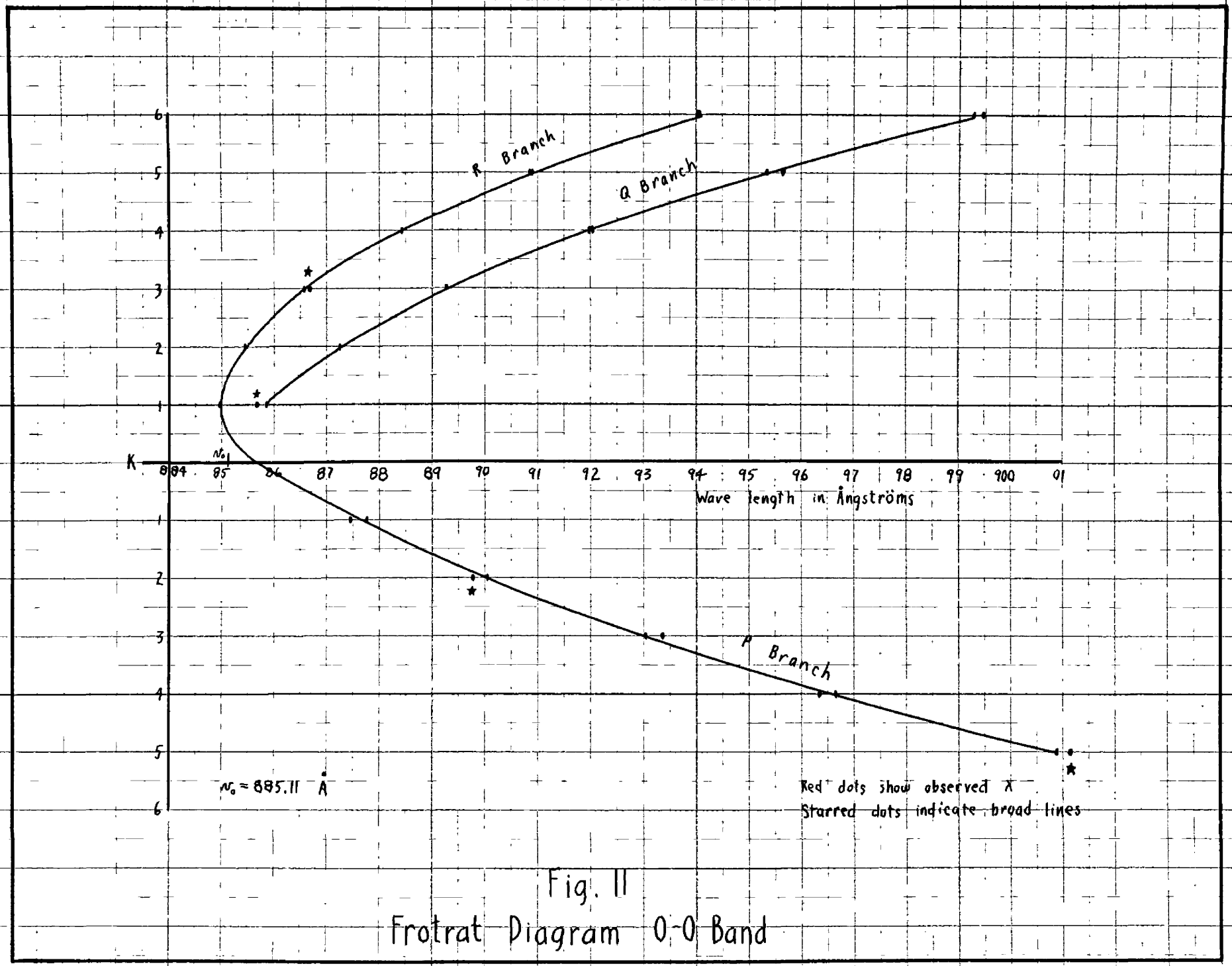

Fig. 11

Frotrat Diagram 0-0 Band

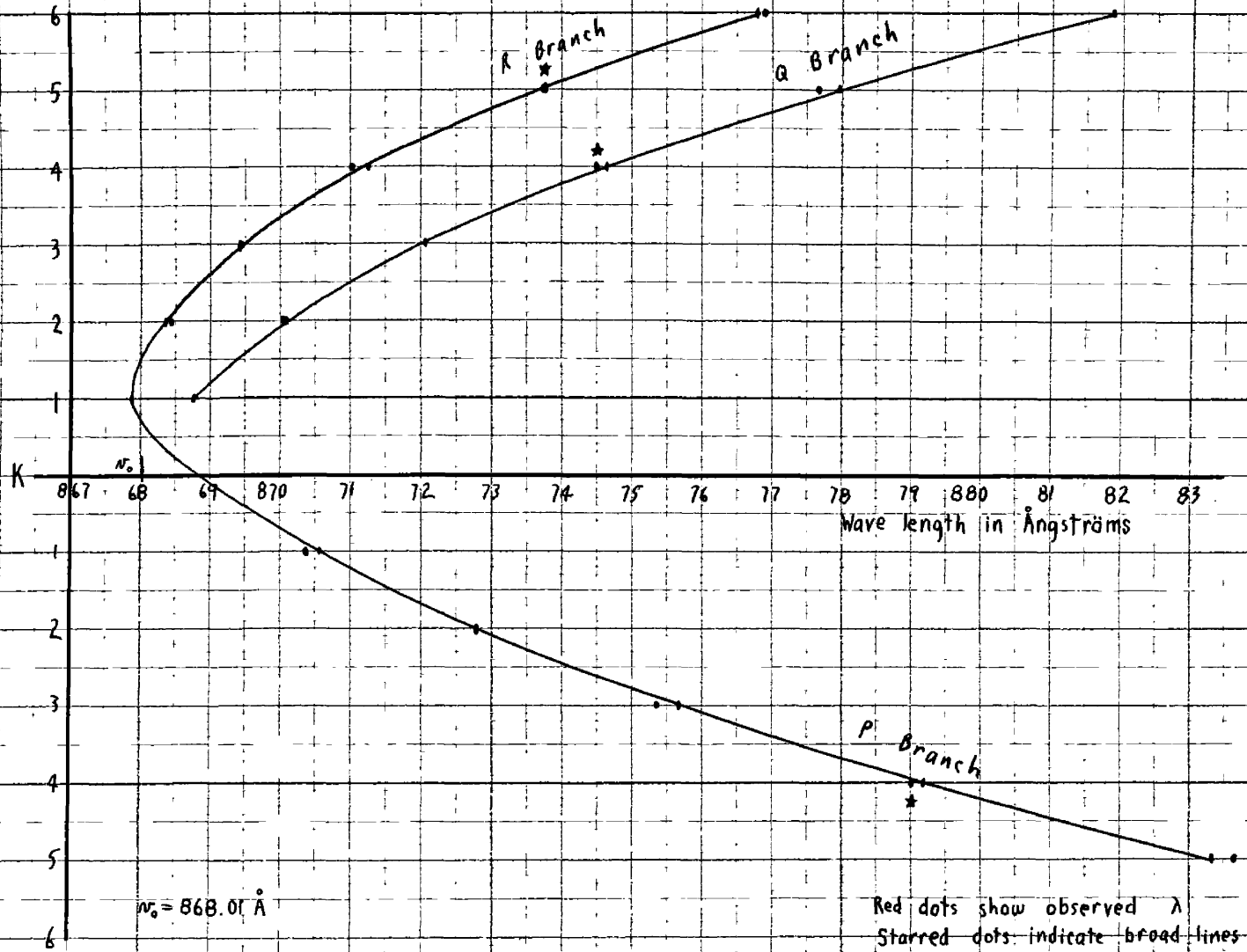

Fig. 12

Frotrat Diagram 1-0 Band

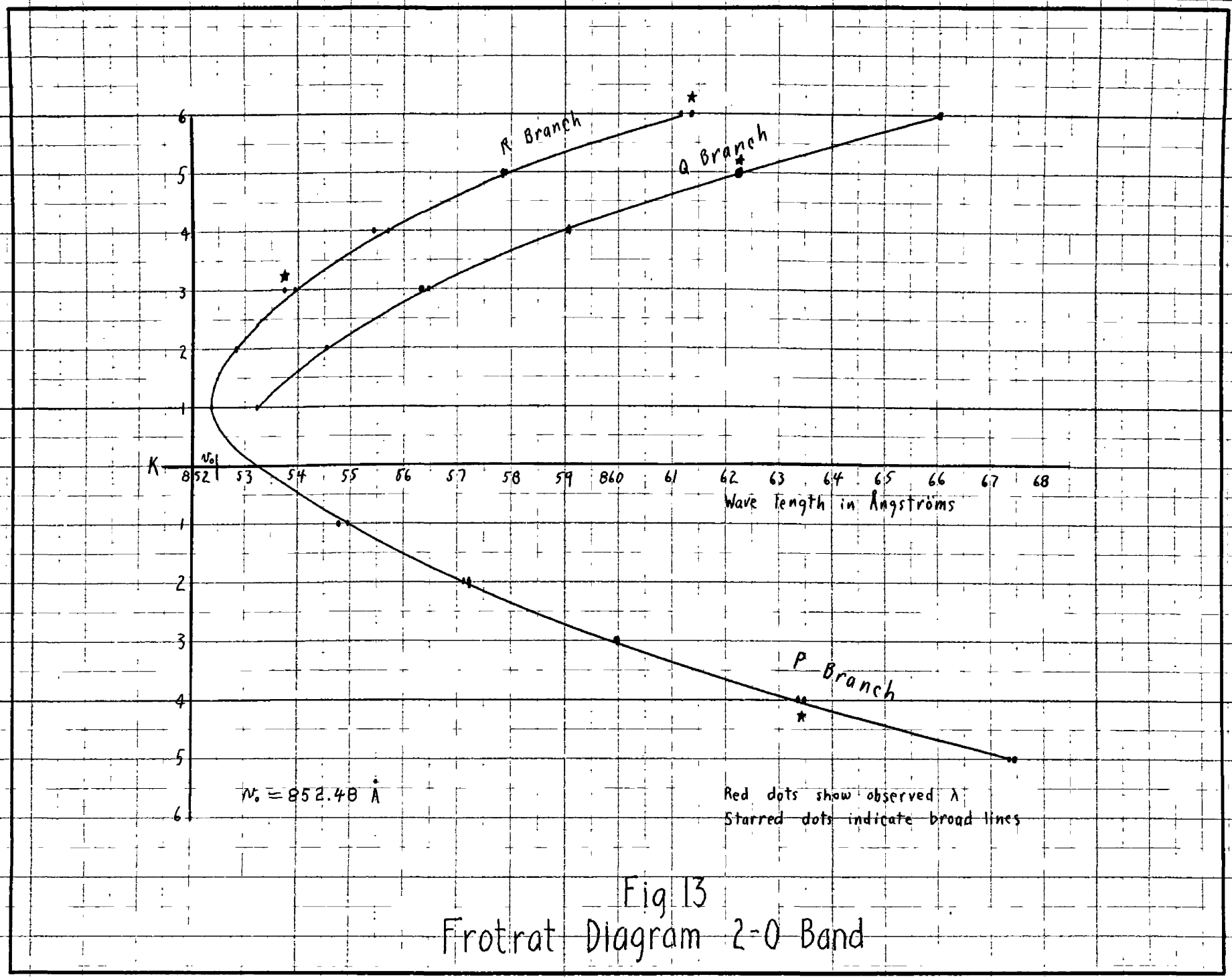

Fig 13

Frotrat Diagram 2-0 Band

BIBLIOGRAPHY

Beutler, Deubner and Junger, Zeits of Physik, 98, 181 (1935).

Beutler and Junger, Zeits f. Physik., 100, 80 (1936).

Boyce, J. C., and H. A. Robinson, "Wave Length Identification. Lists for the Extreme Ultraviolet." Jour. Opt. Soc. Am., 26, 133 (1936).

Collins and Price, "A Source of the Lyman Continuum for use with Spectrographs of High Dispersion." Review of Scien. Inst., 5, 423 (1934).

Hopfield, J. J. and E. T. S. Appleyard, "A Simplified Method of Preparing Schumann Plates", Jour. Opt. Soc. Am., 22, (1932).

Hopfield, J. J. , "New Spectrum of the Hydrogen Molecule.", Nature Magazine 125, 923 (1930).

Jeppesen, C. R., "Emission Bands in the $3p'\Pi_{cd} - 1s'\Sigma$ System of the Hydrogen Molecule", Physical Review 54, 68 (1938)

Richardson, O. W., Molecular Hydrogen and its Spectrum, Yale University Press 1934.

Stewart, O. M., Physics, Textbook for College, Ginn and Co., New York, 1939.